

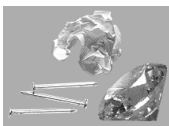
## Chemical Kinetics: The Rates of Chemical Reactions

Chapter 12



An automotive catalytic muffler.

Chemistry 222  
Professor Michael Russell



Last update:  
4/28/24

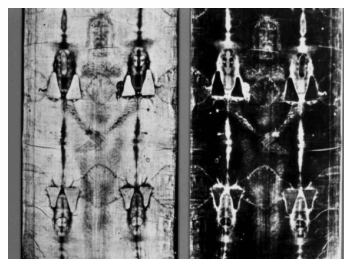
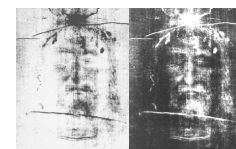
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## Shroud of Turin

Shroud of Jesus?!?

Fake or Real?

Explored with Kinetics



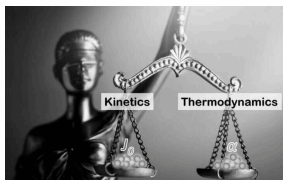
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## Chemical Kinetics

We can use **thermodynamics** to tell if a reaction is product or reactant favored.

But this gives us no info on **HOW FAST** reaction goes from reactants to products.

**KINETICS** - the study of **REACTION RATES** and their relation to the way the reaction proceeds, i.e., its **MECHANISM**.



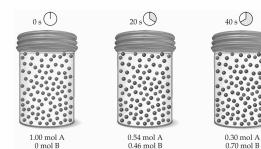
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## Reaction Rates

**Reaction rate** is the change in concentration of a reactant or product with time

Ex: for  $A \rightarrow B$



## Reaction Rates

**Reaction rate** is the change in concentration of a reactant or product with time

**Reactants disappear** with time (hence, negative sign), and **products appear** with time (hence, positive sign)

Ex: for  $N_2O_4(g) \rightarrow 2 NO_2(g)$

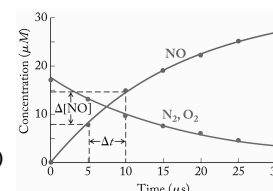
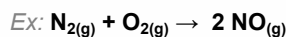
$$rate = -\frac{\Delta[N_2O_4]}{\Delta t} = +\frac{1}{2} \frac{\Delta[NO_2]}{\Delta t}$$

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Rates in chemistry are usually "amount per unit time", i.e. M/s, etc.

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## Reaction Rates

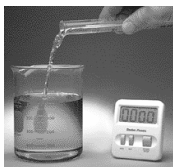


$$Rate \text{ of } N_2 \text{ consumption} = -\frac{\Delta[N_2]}{\Delta t} = -\frac{[N_2]_{\text{final}} - [N_2]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}$$

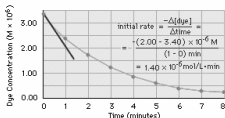
$$Rate \text{ of } O_2 \text{ consumption} = -\frac{\Delta[O_2]}{\Delta t} = -\frac{[O_2]_{\text{final}} - [O_2]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}$$

$$Reaction \text{ Rate} = -\frac{\Delta[N_2]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[NO]}{\Delta t}$$

### Determining a Reaction Rate

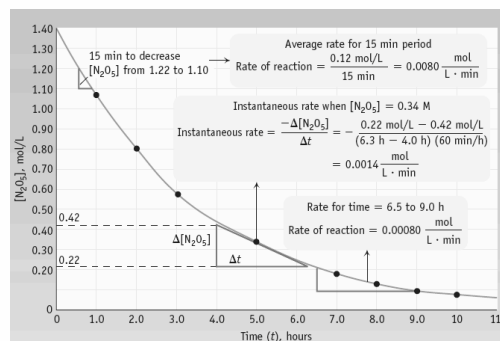


**Blue dye is oxidized with bleach.**  
**Its concentration decreases with time.**  
**The rate - the change in dye conc with time - can be determined from a plot of [Dye] vs. time**



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### Average, Instantaneous, Reaction Rates



We will use "average rate" in CH 22

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### Factors Affecting Rates

#### Concentration

Greater concentration of reactants means more collisions and faster rates

#### Surface Area

Increased surface area means greater chances for collisions and faster rates

#### Temperature

Higher temperatures means particles collide with greater kinetic energy, increasing the rates

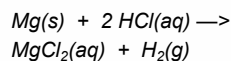
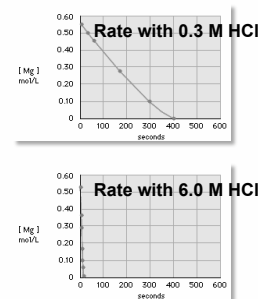
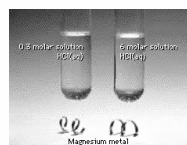
#### Catalysts

Catalysts speed up reactions without being used up. They lower the activation energy and increase the rates

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### Factors Affecting Rates

#### Concentrations



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### Factors Affecting Rates

#### Surface area of reactants

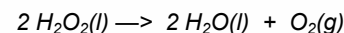


**Lycopodium powder** is a yellow-tan dust-like powder consisting of the dry spores of clubmoss plants or ferns

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### Factors Affecting Rates

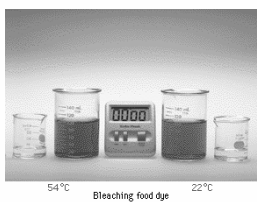
#### Catalysts: catalyzed decomposition of $\text{H}_2\text{O}_2$ with $\text{MnO}_2$



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## Factors Affecting Rates

### Temperature



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## Concentrations and Rates

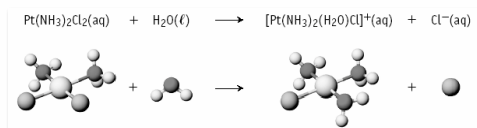
To postulate a reaction mechanism, we study its reaction rate and concentration dependence



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## Concentrations and Rates

Take reaction where Cl<sup>-</sup> in cisplatin [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] is replaced by H<sub>2</sub>O



$$\begin{aligned} \text{Rate of change of conc of Pt compd} \\ = \frac{\text{Am't of cisplatin reacting (mol/L)}}{\text{elapsed time (t)}} \end{aligned}$$

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## Concentrations and Rates

$$\begin{aligned} \text{Rate of change of conc of Pt compd} \\ = \frac{\text{Am't of cisplatin reacting (mol/L)}}{\text{elapsed time (t)}} \end{aligned}$$

If calculated rate =  $4.3 \times 10^{-6} \text{ M s}^{-1}$  and [cisplatin] = 0.00250 M, then **approximate time** for cisplatin to react:

$$\text{rate} = [\text{cisplatin}] / \text{time, and}$$

$$\text{time} = [\text{cisplatin}] / \text{rate}$$

$$\text{time} = 0.00250 \text{ M} / 4.3 \times 10^{-6} \text{ M s}^{-1}$$

$$\text{time} = 580 \text{ s}$$



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## Concentrations and Rates

$$\begin{aligned} \text{Rate of change of conc of Pt compd} \\ = \frac{\text{Am't of cisplatin reacting (mol/L)}}{\text{elapsed time (t)}} \end{aligned}$$

Rate of reaction is **proportional** to [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]

We express this as a **RATE LAW**

$$\text{Rate of reaction} = k [\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$$

where **k** = rate constant

**k** is independent of conc. but increases with T

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## Concentrations, Rates, and Rate Laws

In general, for



$$\text{Rate} = k [\text{A}]^m [\text{B}]^n [\text{C}]^p$$

The exponents **m**, **n**, and **p**

- are the reaction order
- can be 0, 1, or 2 (in CH 222 - CH 223!)
- must be determined by experiment!
- **overall order** = **m** + **n** + **p**

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## Interpreting Rate Laws

**Example: Rate = k [A]<sup>m</sup>**

If m = 1, rxn. is 1st order in A

$$\text{Rate} = k [A]^1$$

If [A] doubles, then rate goes up by factor of ?

If m = 2, rxn. is 2nd order in A.

$$\text{Rate} = k [A]^2$$

Doubling [A] increases rate by ?

If m = 0, rxn. is zero order.

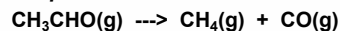
$$\text{Rate} = k [A]^0$$

If [A] doubles, rate ?

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## Deriving Rate Laws

**Example: Derive rate law and k for**



from experimental data for rate of disappearance of CH<sub>3</sub>CHO

Expt.	[CH <sub>3</sub> CHO] (mol/L)	Disappear of CH <sub>3</sub> CHO (mol/L•sec)
1	0.10	0.020
2	0.20	0.081
3	0.30	0.182
4	0.40	0.318

The rate law:  $\text{rate} = k[\text{CH}_3\text{CHO}]^x$

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## Deriving Rate Laws

Expt.	[CH <sub>3</sub> CHO] (mol/L)	Rate of CH <sub>3</sub> CHO (mol/L•sec)
1	0.10	0.020
2	0.20	0.081
3	0.30	0.182
4	0.40	0.318

Let's find the order (x) with respect to CH<sub>3</sub>CHO

Use two trials where [CH<sub>3</sub>CHO] changes - any change in rate is caused by CH<sub>3</sub>CHO

Apply the rate law to these two trials:

$$\begin{array}{l} \text{Rate 2} = \frac{0.081}{0.020} = k(0.20)^x \\ \text{Rate 1} = \frac{0.020}{0.020} = k(0.10)^x \\ 4.1 = 2.0^x \\ 2 = x \end{array} \quad \left\{ \begin{array}{l} \text{Could also:} \\ \log 4.1 = \log 2.0^x = x \log 2.0 \\ x = (\log 4.1) / (\log 2.0) \\ x = 2 \end{array} \right.$$

So the order of reaction for CH<sub>3</sub>CHO is "2". We say the reaction is second order with respect to CH<sub>3</sub>CHO

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## Deriving Rate Laws

Rate of rxn = k [CH<sub>3</sub>CHO]<sup>2</sup>

Here the rate goes up by \_\_\_\_\_ when initial conc. doubles. Therefore, we say this reaction is \_\_\_\_\_ order.

Now determine the value of k. Use expt. #3 data on earlier slide,

$$0.182 \text{ mol/L}\cdot\text{s} = k (0.30 \text{ mol/L})^2$$

$$k = 2.0 \text{ (L / mol}\cdot\text{s)}$$

Using k you can calc. rate at other values of [CH<sub>3</sub>CHO] at same T.

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## Concentration/Time Relations

Chemists need to know what the concentration of reactant is as function of time.

Most reactions are first order (radioactive, biological, etc.)

Let's consider FIRST ORDER REACTIONS

For 1st order reactions (1), the rate law is:

$$-(\Delta [R] / \Delta \text{time}) = k [R]^1$$

Integration (calculus):  $\int_0^t \frac{1}{[R]} dR = -k \int_0^t dt$

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## Concentration/Time Relations

Integrating  $-(\Delta [R] / \Delta \text{time}) = k [R]$  we get:

$$\ln \frac{[R]_t}{[R]_0} = -kt$$

natural logarithm [R] at time = 0

[R]<sub>t</sub> / [R]<sub>0</sub> = fraction remaining after time t has elapsed.

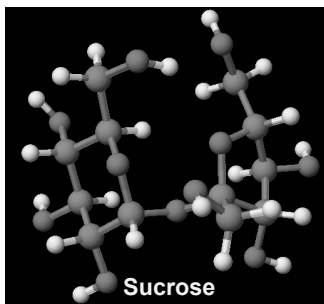
This is the integrated first-order rate law.

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### Concentration/Time Relations



Sucrose decomposes to simpler sugars

Rate of disappearance of sucrose =  $k$  [sucrose]

$k = 0.21 \text{ hr}^{-1}$

Initial [sucrose] = 0.010 M

How long to drop 90% (to 0.0010 M)?

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### Concentration/Time Relations

Rate of disappear of sucrose =  $k$  [sucrose],  $k = 0.21 \text{ hr}^{-1}$ . If initial [sucrose] = 0.010 M, how long to drop 90% or to 0.0010 M?

Use the first order integrated rate law

$$\ln \left( \frac{0.0010 \text{ M}}{0.010 \text{ M}} \right) = - (0.21 \text{ hr}^{-1}) t$$

$$\ln (0.10) = - 2.30 = - (0.21 \text{ hr}^{-1}) \cdot \text{time}$$

$$\text{time} = 11 \text{ hours}$$

sig figs and logarithms covered in CH 223

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### Using the Integrated Rate Law

The integrated rate law suggests a way to tell if a reaction is first order based on experiment.

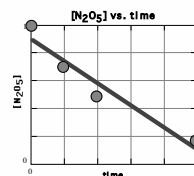
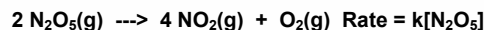


Rate =  $k[\text{N}_2\text{O}_5]$

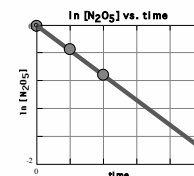
Time (min)	[N <sub>2</sub> O <sub>5</sub> ] (M)	ln [N <sub>2</sub> O <sub>5</sub> ]
0	1.00	0
1.0	0.705	-0.35
2.0	0.497	-0.70
5.0	0.173	-1.75

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### Using the Integrated Rate Law



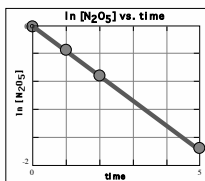
Data of conc. vs. time plot do not fit straight line.



Plot of ln [N<sub>2</sub>O<sub>5</sub>] vs. time is a straight line!

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### Using the Integrated Rate Law



Plot of ln [N<sub>2</sub>O<sub>5</sub>] vs. time is a straight line!  
Eqn. for straight line:  $y = ax + b$

$$\ln [\text{N}_2\text{O}_5] = -kt + \ln [\text{N}_2\text{O}_5]_0$$

↑ conc at time t     ↑ rate const = slope     ↑ conc at time = 0

All 1st order reactions have straight line plot for ln [R] vs. time.

(2nd order gives straight line for plot of 1/[R] vs. time; zero order [R] vs. time) - see [Handout](#)

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### Using the Rate Laws

Characteristic Properties of Reactions of the Type "R → Products"					
Order	Rate Equation	Integrated Rate Equation	Straight-Line Plot	Slope	k Units
0	$-\Delta[\text{R}]/\Delta t = k[\text{R}]^0$	$[\text{R}]_t - [\text{R}]_0 = kt$	[R] <sub>t</sub> vs. t	-k	mol/L · time
1	$-\Delta[\text{R}]/\Delta t = k[\text{R}]^1$	$\ln([\text{R}]_t/[\text{R}]_0) = -kt$	ln [R] <sub>t</sub> vs. t	-k	time <sup>-1</sup>
2	$-\Delta[\text{R}]/\Delta t = k[\text{R}]^2$	$(1/[\text{R}]_t) - (1/[\text{R}]_0) = kt$	1/[R] <sub>t</sub> vs. t	k	L/mol · time

Also see the ["Kinetics Cheat Sheet" Handout](#)

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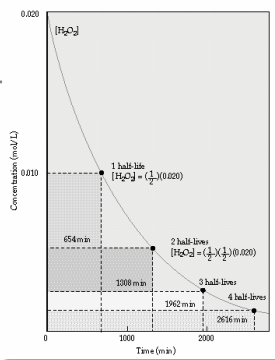
### Half-Life

**HALF-LIFE** is the time it takes for 1/2 a sample is disappear.

$$\frac{N_t}{N_0} = 0.5^n$$

$n$  = the number of half-lives

For 1st order reactions, the concept of **HALF-LIFE** is especially useful.

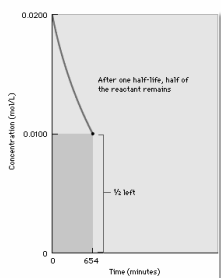
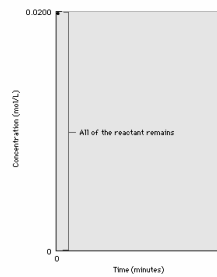


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### Half-Life

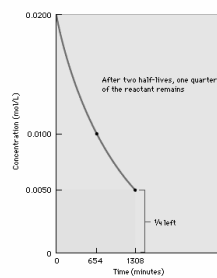
Reaction is 1st order decomposition of  $H_2O_2$ .



### Half-Life

Reaction after 654 min, 1 half-life.  
1/2 of the reactant remains.

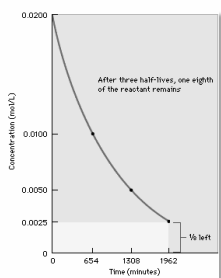
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### Half-Life

Reaction after 1308 min, or 2 half-lives.  
1/4 of the reactant remains.

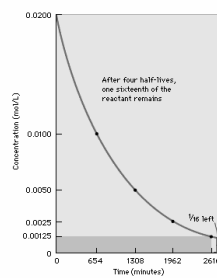
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### Half-Life

Reaction after 3 half-lives, or 1962 min.  
1/8 of the reactant remains.

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### Half-Life

Reaction after 4 half-lives, or 2616 min.  
1/16 of the reactant remains.

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## Half-Life

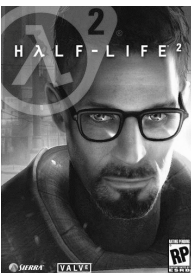
Sugar is fermented in a 1st order process (using an enzyme as a catalyst).

sugar + enzyme  $\rightarrow$  products

Rate of disappear of sugar =  $k[\text{sugar}]$

$$k = 3.3 \times 10^{-4} \text{ sec}^{-1}$$

What is the half-life of this reaction?



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## Half-Life

Rate =  $k[\text{sugar}]$  and  $k = 3.3 \times 10^{-4} \text{ sec}^{-1}$ . What is the half-life of this reaction?

Solution

$$[R] / [R]_0 = 1/2 \text{ when } t = t_{1/2}$$

$$\text{Therefore, } \ln(1/2) = -k \cdot t_{1/2}$$

$$-0.693 = -k \cdot t_{1/2}$$

$$t_{1/2} = 0.693 / k$$

So, for sugar,

$$t_{1/2} = 0.693 / k = 2100 \text{ sec} = 35 \text{ min}$$

see Handout

## Half-Life

Rate =  $k[\text{sugar}]$  and  $k = 3.3 \times 10^{-4} \text{ sec}^{-1}$ . Half-life is 35 min. Start with 10.00 g sugar. How much is left after 2 hr and 20 min? ( $t_{1/2} = 0.693 / k$ )

Two Solution pathways - The "CH 104" method:

2 hr and 20 min = 4 half-lives

Half-life	Time Elapsed	Mass Left
1st	35 min	5.00 g
2nd	70	2.50 g
3rd	105	1.25 g
4th	140	0.625 g answer

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## Half-Life

Rate =  $k[\text{sugar}]$  and  $k = 3.3 \times 10^{-4} \text{ sec}^{-1}$ . Half-life is 35 min. Start with 10.00 g sugar. How much is left after 2 hr and 20 min? ( $t_{1/2} = 0.693 / k$ )

Two Solution Pathways - The "CH 222" Method:

Convert 2 hrs 20 min to 8400 seconds

$$\ln(R / 10.00 \text{ g}) = -(3.3 \times 10^{-4} \text{ sec}^{-1})(8400 \text{ s})$$

$$\ln(R / 10.00 \text{ g}) = -2.772$$

$$\text{Take antilog: } (R / 10.00 \text{ g}) = e^{-2.772} = 0.0625$$

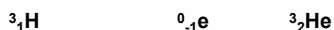
$$R = 10.00 \text{ g} \cdot 0.0625 = 0.625 \text{ g}$$

CH 222 Method recommended,  
not limited to whole number of half-lives, etc.  
 $e =$  "Euler's number" in math = 2.71828...

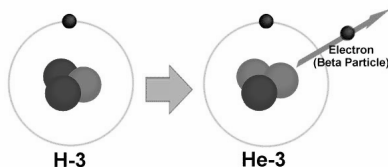
## Half-Life

Radioactive decay is a first order process.

Tritium  $\rightarrow$  electron + helium



If you have 1.50 mg of tritium, how much is left after 49.2 years?  $t_{1/2} = 12.3 \text{ years}$



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## Half-Life

Start with 1.50 mg of tritium, how much is left after 49.2 years?  $t_{1/2} = 12.3 \text{ years}$

$$\ln [R] / [R]_0 = -kt$$

$$[R] = ? \quad [R]_0 = 1.50 \text{ mg} \quad t = 49.2 \text{ yrs}$$

$$\text{Need } k, \text{ so we calc } k \text{ from: } k = 0.693 / t_{1/2}$$

$$\text{Obtain } k = 0.0564 \text{ y}^{-1}$$

$$\text{Now } \ln [R] / [R]_0 = -kt = -(0.0564 \text{ y}^{-1}) \cdot (49.2 \text{ y}) = -2.77$$

$$\text{Take antilog: } [R] / [R]_0 = e^{-2.77} = 0.0627$$

0.0627 is the fraction remaining

$$[R]_0 = 1.50 \text{ mg, so } [R] = 1.50 \cdot 0.0627 = 0.0941 \text{ mg}$$

### Half-Life

Half-Life for first order reactions:

$$t_{1/2} = 0.693 / k$$

All biological, radioactive processes first order, most useful

Half-Life for second order reactions:

$$t_{1/2} = 1 / (k[A]_0)$$

Half-Life for zero order reactions:

$$t_{1/2} = [A]_0 / 2k$$

$[A]_0$  is the initial concentration of the reactant

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### Half-Lives of Radioactive Elements

Rate of decay of radioactive isotopes given in terms of half-life ( $t_{1/2}$ ).

$^{238}\text{U} \rightarrow ^{234}\text{Th} + \text{He}$	4.5 x 10 <sup>9</sup> y
$^{14}\text{C} \rightarrow ^{14}\text{N} + \text{beta}$	5730 y
$^{131}\text{I} \rightarrow ^{131}\text{Xe} + \text{beta}$	8.05 d
<b>Element 106 - seaborgium</b>	
$^{263}\text{Sg} \rightarrow ^{259}\text{Rf} + \text{He}$	0.8 s
<b>Element 111 - roentgenium</b>	
$^{272}\text{Rg} \rightarrow ^{268}\text{Mt} + \text{He}$	0.0015 s

Half-life also used in medicine;  
 $t_{1/2}$  caffeine = 3.5 hours in the body

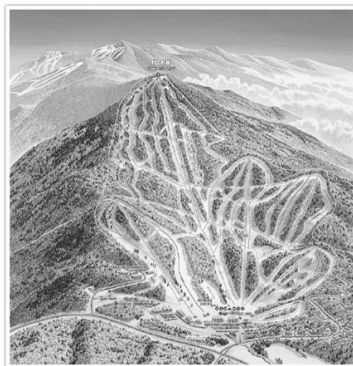
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### MECHANISMS

A Microscopic View of Reactions

How are reactants converted to products at the molecular level?

We want to connect the RATE LAW to the MECHANISM the experiment to the theory

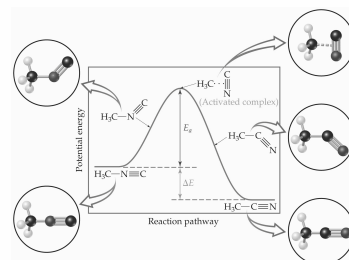


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### Reaction Coordinate Diagrams

It is helpful to visualize energy changes throughout a process on a reaction coordinate diagram.

This diagram shows the rearrangement of methyl isocyanide to methyl cyanide (acetonitrile).



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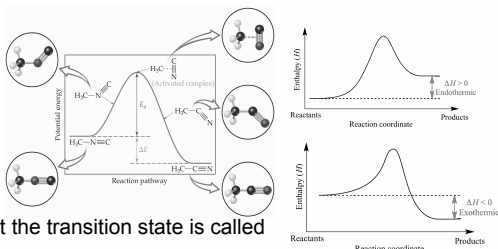
### Reaction Coordinate Diagrams

The diagram shows the energy of the reactants and products (and, therefore,  $\Delta E$ ); *exo*- or *endo*-thermic!

The high point on the diagram is the transition state.

The species present at the transition state is called the activated complex.

The energy gap,  $E_a$  between the reactants and the activated complex is the activation energy barrier.



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### Activation Energy

There is a minimum amount of energy required for a reaction: the activation energy,  $E_a$ .

In general, differences in activation energy are the reason reactions vary from fast to slow.

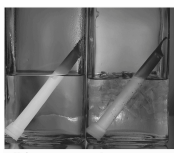


An analogy to chemical activation energy. In order for the volleyball to go over the net, the player must give it sufficient energy.



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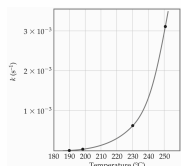
## Temperature and Rate



Generally, as temperature increases, so does the reaction rate.

This is because  $k$  is temperature dependent.

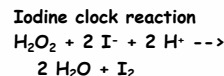
Find activation energy through changes in temperature.



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## Effect of Temperature

Reactions generally occur slower at lower T.

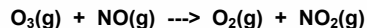


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## Collision Theory

To break and make bonds, reactions require

- (a) activation energy and
- (b) correct geometry.



Insufficient activation energy



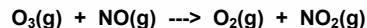
Incorrect geometry

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## Collision Theory

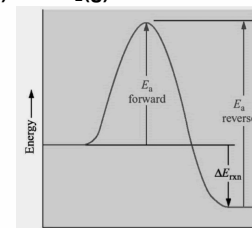
To break and make bonds, reactions require

- (a) activation energy and
- (b) correct geometry.



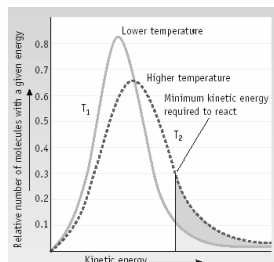
Correct activation energy and geometry

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## Activation Energy and Temperature

Reactions are slower at lower T because a smaller fraction of reactant molecules have enough energy to convert to product molecules.



In general, differences in activation energy cause reactions to vary from fast to slow.

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Svante Arrhenius

## The Arrhenius Equation

Arrhenius equation -

$$\text{Rate constant } k = A e^{-E_a/RT}$$

Labels:  $A$  is Frequency factor;  $E_a$  is Activation energy;  $R$  is 8.3145 J/K·mol;  $T$  is Temp (K).

Frequency factor = frequency of collisions with correct geometry.

Plot  $\ln k$  vs.  $1/T \rightarrow$  straight line.  
 slope =  $-E_a/R$ ,  
 best way to find  $E_a$

$$\ln k = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

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Always use 8.3145 for "energy" R!

### More About the Frequency Factor, A

Frequency Factor often expressed as:

$$A = e^{\left(\frac{k_B T}{h}\right)} e^{\left(\frac{\Delta S^\ddagger}{R}\right)}$$

Labels in diagram:  
 Boltzmann constant,  $1.381 \times 10^{-23} \text{ J/K}$   
 Temp (K)  
 Planck constant,  $6.626 \times 10^{-34} \text{ J s}$   
 Entropy of activation,  $8.3145 \text{ J/K}\cdot\text{mol}$

We will be seeing entropy ( $\Delta S$ ) again in CH 223.

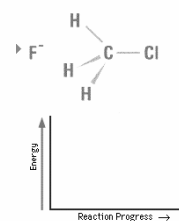
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### REACTION MECHANISMS

A reaction mechanism is the sequence of events that describes the actual process by which reactants become products.

Reactions may occur all at once ("single step") or through several discrete steps.

Each of these steps known as an elementary step



A bimolecular reaction  
Exo- or endothermic?

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### MOLECULARITY

The molecularity of a process tells how many molecules are involved in the elementary step.

**UNIMOLECULAR** - only one reactant is involved.

**BIMOLECULAR** - two different molecules must collide

**TERMOLECULAR** - three different molecules collide

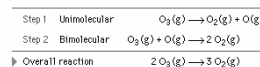
Molecularity	Elementary Reaction	Rate Law
Unimolecular	$A \rightarrow \text{products}$	$\text{Rate} = k[A]$
Bimolecular	$A + A \rightarrow \text{products}$	$\text{Rate} = k[A]^2$
Bimolecular	$A + B \rightarrow \text{products}$	$\text{Rate} = k[A][B]$
Termolecular	$A + A + A \rightarrow \text{products}$	$\text{Rate} = k[A]^3$
Termolecular	$A + A + B \rightarrow \text{products}$	$\text{Rate} = k[A]^2[B]$
Termolecular	$A + B + C \rightarrow \text{products}$	$\text{Rate} = k[A][B][C]$

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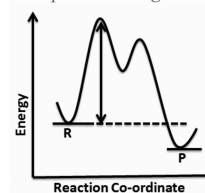
### MECHANISMS

Some reactions occur in a single elementary step. **Most** reactions involve a sequence of elementary steps.

Adding elementary steps gives **NET** reaction.



Every elementary step gets a "hump" in the diagram



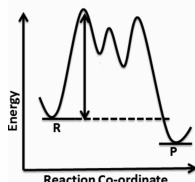
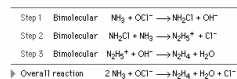
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### MECHANISMS

Most reactions involve a **sequence** of elementary steps.

Adding elementary steps gives **NET** reaction.

Every elementary step gets a "hump" in the diagram

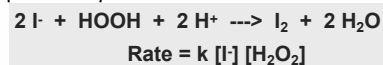


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### Mechanisms

In multistep mechanisms, one step will be slower than all others - this is the **rate determining step** (rds).

Most reactions involve a sequence of elementary steps. **Example:**



Note that the **rate law** comes from experiment.

Also note that **order of reactants** in rate law **not necessarily the same as stoichiometric coefficients!**

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## MECHANISMS



$$\text{Rate} = k [\text{I}^-] [\text{HOOH}]$$

A scientist proposes the following mechanism for this reaction:



Note that  $\text{H}^+$  not involved in slow step, so  $[\text{H}^+]$  is not in the rate law (a zero order reactant.)

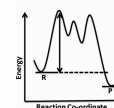
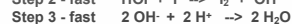
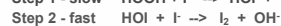
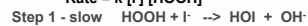
Bimolecular slow step reflected in the rate law; this is a legitimate mechanism.

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## MECHANISMS



$$\text{Rate} = k [\text{I}^-] [\text{HOOH}]$$



Step 1 is bimolecular and involves  $\text{I}^-$  and  $\text{HOOH}$ .

Therefore, this predicts the rate law should be

**Rate  $\propto [\text{I}^-] [\text{HOOH}]$  - as observed!!**

The species **HOI** and **OH<sup>-</sup>** are **reaction intermediates**; critical for providing evidence for or against a proposed mechanism.

See: [Reaction Mechanisms Guide](#)

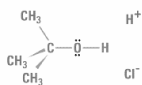
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## Mechanisms - Uses

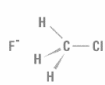
Mechanisms help predict the products of a reaction

Very useful in organic chemistry: the  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  mechanisms

$\text{S}_{\text{N}} = \text{substitution nucleophilic}$



$\text{S}_{\text{N}}1$

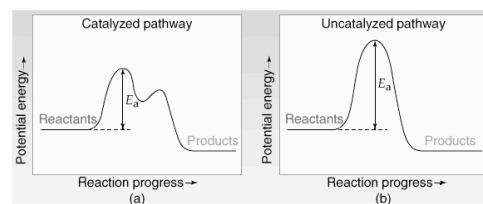


$\text{S}_{\text{N}}2$

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## CATALYSIS

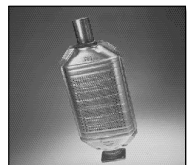
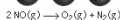
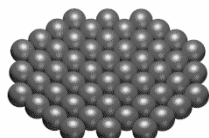
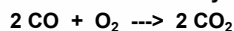
Catalysts speed up reactions by altering the mechanism to lower the activation energy barrier.



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## CATALYSIS - Uses

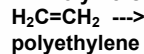
1. In auto exhaust systems - Pt, NiO, PtO



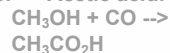
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## CATALYSIS - Uses

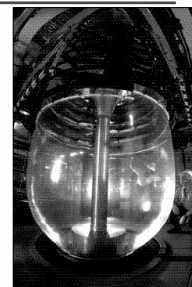
2. Polymers:



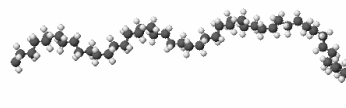
3. Acetic acid:



4. Enzymes - biological catalysts



Making polyethylene film



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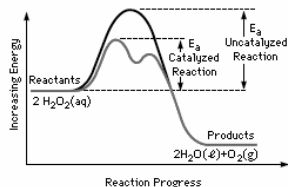


## CATALYSIS

### Catalysis and activation energy



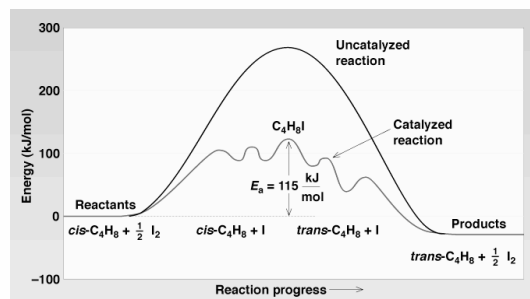
**MnO<sub>2</sub> catalyzes decomposition of H<sub>2</sub>O<sub>2</sub>**  
 $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$



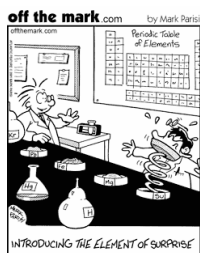
— Uncatalyzed reaction  
 — Catalyzed reaction

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### Iodine-Catalyzed Isomerization of cis-2-Butene



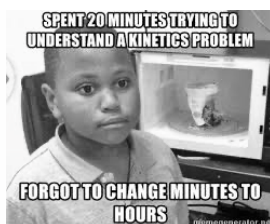
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### End of Chapter 12

See:

- [Chapter Twelve Study Guide](#)
- [Chapter Twelve Concept Guide](#)
- [Important Equations \(following this slide\)](#)
- [End of Chapter Problems \(following this slide\)](#)



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### Important Equations, Constants, and Handouts from this Chapter:

The Rate Law:

$$\text{Rate} = k[\text{A}]^p[\text{B}]^m[\text{C}]^n \dots$$

$m, n, p = 0, 1 \text{ or } 2 \text{ only (in our classes)}$

1st Order Integrated Rate Law:

$$\ln \frac{[\text{R}]}{[\text{R}_0]} = -kt$$

$$t_{1/2} = \frac{0.693}{k}$$

The Arrhenius Equation:

$$\ln(k) = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln(A)$$

- $R = 8.3145 \text{ J/mol}\cdot\text{K}$
- "Kinetics Cheat Sheet" handout
- "Reactions Mechanisms" handout

**Kinetics:** rate, rate law, orders of reaction, the rate constant ( $k$ ), 1st vs. 2nd. vs. zero order, half life, mechanism, elementary reaction, bimolecular (and uni- and ter-molecular), Arrhenius equation, activation energy, frequency factor, mechanism, intermediate, catalyst, rds (rate determining step)

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### End of Chapter Problems: Test Yourself

1. The reaction between ozone and nitrogen dioxide at 231 K is first order in both NO<sub>2</sub> and O<sub>3</sub>:  $2 \text{NO}_2(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{N}_2\text{O}_5(\text{s}) + \text{O}_2(\text{g})$ . Write the rate equation for the reaction. If the concentration of NO<sub>2</sub> is tripled, what is the change in the reaction rate?
2. After 2.57 h at 27 °C, a first order sucrose concentration decreased from 0.0146 M to 0.0132 M. Find the rate constant,  $k$ .
3. The compound Xe(CF<sub>3</sub>)<sub>2</sub> decomposes in a first-order reaction to elemental Xe with a half-life of 30. min. If you place 7.50 mg of Xe(CF<sub>3</sub>)<sub>2</sub> in a flask, how long must you wait until only 0.25 mg of Xe(CF<sub>3</sub>)<sub>2</sub> remains?
4. Gaseous NO<sub>2</sub> decomposes at 573 K:  $2 \text{NO}_2(\text{g}) \rightarrow 2 \text{NO}(\text{g}) + \text{O}_2(\text{g})$ . The concentration of NO<sub>2</sub> was measured as a function of time. A graph of  $1/[\text{NO}_2]$  versus time gives a straight line with a slope of 1.1 L/mol·s. What is the rate law for this reaction? What is the rate constant  $k$ ?
5. What is the rate law for the following elementary reaction:  $\text{NO}(\text{g}) + \text{NO}_3(\text{g}) \rightarrow 2 \text{NO}_2(\text{g})$
6. For a reaction,  $\ln k$  versus  $1/T(\text{K})$  is plotted, and the linear regression line is:  $y = -6373.3x + 18.19$ ,  $r = -0.997$ . What is the activation energy for this reaction?

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### End of Chapter Problems: Answers

1.  $\text{Rate} = k[\text{NO}_2][\text{O}_3]$ ; tripling NO triples the rate.
2.  $0.0392 \text{ h}^{-1}$
3. 150 min
4.  $\text{Rate} = k[\text{NO}_2]^2$ ,  $k = 1.1 \text{ L/mol}\cdot\text{s}$
5.  $\text{Rate} = k[\text{NO}][\text{NO}_3]$
6. 53.0 kJ/mol

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